

Isobaric Critical Exponents: Test of Analyticity against NIST Reference Data

Wonyoung Cho[‡], Do-Hyun Kim^{‡,*}, and Jeong-Hyuck Park^{‡,†,*}

[‡]*Department of Physics, Sogang University, 35 Baekbeom-ro, Mapo-gu, Seoul 04107, Korea*

[†]*B. W. Lee Center for Fields, Gravity and Strings, Institute for Basic Science, Daejeon 34047, Korea*

The conventional paradigm for critical phenomena typically assumes the thermodynamic limit in order to achieve non-analyticity. Yet, a counterexample based on the ‘analyticity’ of a finite-system partition function has been suggested. It relies solely on the existence of a spinodal curve and predicts universal values for *isobaric critical exponents*, α_P , β_P and γ_P , which are some exponents defined in an analogous manner to the usual ones except that the critical point is approached *via* isobaric transformations. Here we analyze the high-precision NIST experimental data for twenty major molecules, including H₂O, O₂, CO₂, *etc.* We report that they are in good agreement with the latter analytic prediction, at least for the temperature range of $|T/T_c - 1| < 10^{-3}$. For each molecule, there exists a characteristic natural number, $n = 2, 3, 4, 5, 6$, which determines all the critical exponents for $T < T_c$ as $\alpha_P = \gamma_P = \frac{n}{n+1}$ and $\beta_P = \delta^{-1} = \frac{1}{n+1}$. For the opposite $T > T_c$, all the fluids feature the universal value of $n = 2$. These critical exponents satisfy both Rushbrooke and Widom scaling laws. We also point out that van der Waals fluid belongs to the class of $n = 2$.

INTRODUCTION

The celebrated paradigm for critical phenomena in modern statistical physics typically assumes the thermodynamic limit [1] with the intention of achieving non-analyticity [2]. In this way, correlation length diverges at the critical point, which gives rise to the scaling theory of criticality. In order to describe the scaling, renormalization group methods were developed as for a mathematical framework, *e.g.* [3–11]. Yet, the conventional wisdom asserting that the thermodynamic limit for non-analyticity is a necessary condition to realize phase transitions does not apply to the isobaric situation [12–14] and a counterexample based on the ‘analyticity’ of a finite-system partition function has been suggested [15], which predicts its own universal values for isobaric critical exponents.

In order to boil water while heating, one may better keep the pressure constant, rather than fix the density and take the thermodynamic limit. In the low energy regime, the particle number, N , is conserved, and thus fixing the density is equivalent to keeping the volume constant. In statistical physics, the partition function, $Z_N(T, V)$, is the sum of Boltzmann factors, where the energy eigenvalues are generically quantized with respect to the volume of the system. One crucial difference between volume, V , and pressure, P , is then that the former is a *fundamental variable* of the partition function along with

temperature, T , while the latter is a *conjugate variable* derivable from the partition function, which is *a priori* a single-valued function of the two continuous fundamental variables: $P(T, V)$.

For finite $N \ll \infty$, the partition function is analytic, and hence, changing the temperature alone leaving the volume fixed cannot generate any singularity nor a discrete phase transition. To do so, the conventional statistical physics paradigm suggests to take the thermodynamic limit, $V \rightarrow \infty$ with the density, N/V , fixed. Yet, an alternative scheme has been also around in the literature, prescribing to keep *not* the density *but* the pressure constant, notably by London already in 1954 [12] (see also [13, 14]). The pressure, not as the fundamental but as the conjugate variable, is to be fixed while the system undergoes any discrete phase transition.

In fact, under constant pressure condition, the analytic partition function of a finite system can feature a discrete phase transition provided the volume becomes a multi-valued “function” of T and P . This happens when the partition function features a spinodal curve, which is defined to be the collection of all the points on the (T, V) plane where the isothermal compressibility becomes infinite, or

$$\Phi(T, V) := -\frac{\partial P(T, V)}{\partial V} = 0. \quad (1)$$

Equivalently, the second volume derivative of the free energy vanishes on the spinodal curve (*e.g.* [16–21]), which

thus marks out the frontier of local stability. Crucially, on the spinodal curve, the temperature derivative at fixed pressure acting on an arbitrary physical quantity which is a function of T and V diverges, since the isobaric derivative contains the inverse, Φ^{-1} ,

$$\begin{aligned} \left. \frac{d}{dT} \right|_P &= \left. \frac{\partial}{\partial T} \right|_V + \left. \frac{dV}{dT} \right|_P \left. \frac{\partial}{\partial V} \right|_T \\ &= \left. \frac{\partial}{\partial T} \right|_V + \frac{\frac{\partial P(T,V)}{\partial T}}{\Phi(T,V)} \left. \frac{\partial}{\partial V} \right|_T. \end{aligned} \quad (2)$$

The existence of the spinodal curve for a given analytic partition function of a finite system has been verified: the standard textbook systems of ideal Bose gas feature a spinodal curve, only if the number of the identical particles is sufficiently yet finitely large [15, 22–25]. Small perturbations due to extra interactions may well deform the shape of the spinodal curve but hardly eliminate its existence. In the present paper, we test the theoretical assertion that the spinodal curve exists, or emerges [25], even for a generic interacting system with finitely many particles, or *real molecules*, while the corresponding partition function is analytic. Under this assumption, it follows that, *the isothermal compressibility (or, equivalently, the inverse of Φ)* is the only source of divergence when the isobaric derivative (2) acts on a physical quantity which is an analytic function of T and V . This essentially implies that the corresponding exponent of the singularity in such an isobaric situation is determined by the power series expansion of Φ in a simple manner: the isobaric scaling behavior near a critical point, (T_c, V_c) , can be classified by a natural number which fixes the isobaric critical exponents in a universal and analytic manner, as we review below.

As for the main result of this work, we analyze the commercially available experimental data from “NIST Reference Fluid Thermodynamic and Transport Properties Database (REFPROP)” [26], which has been regarded as the world-best dataset for various fluids. The data are sufficiently precise even close to the critical points: the uncertainties for most fluids do not exceed 2% [27]. We believe that such high-precision data were not available while the conventional paradigm of taking the thermodynamic limit and achieving non-analyticity was proposed and established during the mid 20th century. In particular, the isothermal relation between pressure and

volume appears to have been rather poorly measured, *e.g.* [4]. Among numerous molecules, we focus on twenty major molecules including H_2O , O_2 , CO_2 , *etc.* and report that their critical exponents are in good agreement with the theoretical prediction based on analyticity: for each molecule, there is a characteristic natural number, $n = 2, 3, 4, 5, 6$, which determines all the critical exponents for $T < T_c$ as $\alpha_P = \gamma_P = \frac{n}{n+1}$ and $\beta_P = \delta^{-1} = \frac{1}{n+1}$. For the opposite $T > T_c$, all the fluids feature the universal value of $n = 2$.

GENERAL THEORY

We start with the canonical partition function, $Z_N(T, V)$, of a generic N -particle system. For finite $N < \infty$, the partition function is an *analytic* function of the two continuous variables, T and V . The temperature dependence originates from the Boltzmann factor, $e^{-\beta E}$ with $\beta = (k_B T)^{-1}$, and the volume dependence arises due to the fact that the energy eigenvalues are quantized with respect to the size of the system. Naturally, all the physical quantities computable from the partition function are *a priori* functions of T and V too. For example, the pressure is given by

$$P(T, V) = k_B T \frac{\partial \ln Z_N(T, V)}{\partial V}. \quad (3)$$

It follows infinitesimally,

$$dP = \frac{\partial P(T, V)}{\partial T} dT + \frac{\partial P(T, V)}{\partial V} dV, \quad (4)$$

and hence with the pressure kept fixed, *i.e.* on an isobar, we get

$$\left. \frac{dT}{dV} \right|_P = - \left(\frac{\partial P(T, V)}{\partial V} \right) \left(\frac{\partial P(T, V)}{\partial T} \right)^{-1}. \quad (5)$$

The spinodal curve (1) is defined to be the collection of all the points on the (T, V) plane where the partial volume derivative of the pressure vanishes. Physically, it corresponds to the boundary between the thermodynamically stable points, $\Phi > 0$, and the unstable points, $\Phi < 0$. The existence of a spinodal curve may not be always guaranteed for a given (analytic) partition function. Yet, it has been shown, first numerically [15, 22] and then through analytic approximation [23, 24] that, standard textbook systems of ideal Bose gas feature a spinodal

curve, and hence the isobar on the (T, V) plane zigzags, if the number of particles is sufficiently large: specifically $N \geq 7616$ for the 3D cubic box or $N \geq 35131$ for the 2D square box. Surely, these dimensionless critical numbers of particles are mathematically rather unnatural: the natural one would have been ∞ , *i.e.* the thermodynamic limit. But, they are quantum mechanically generated and determined characteristics of ‘cube’ and ‘square’, *i.e.* the geometric shape of the box. Further, their existence is anyhow physically natural, as no experiment deals a genuinely infinite system. Extra perturbative interaction may well change the dimensionless critical numbers and the shapes of the spinodal curves. Yet, what matters is the appearance of a spinodal curve for large enough N [28]. Hereafter, even for a generic interacting real system with finitely many particles, we shall assume, merely that the spinodal curve exists or emerges, and further tactically that the temperature derivative of the pressure does not vanish (at least) on the spinodal curve,

$$\left. \frac{\partial P(T, V)}{\partial T} \right|_{\Phi=0} \neq 0. \quad (6)$$

It follows from (5) that $\left. \frac{dT}{dV} \right|_P$ vanishes on the spinodal curve, such that the isothermal line ($dT = 0$, $dV \neq 0$) is tangent to the isobar ($dP = 0$). This is also consistent with the definition of the spinodal curve (1).

Crucially, on the spinodal curve, the temperature derivative at fixed pressure acting on an arbitrary physical quantity which is a function of temperature and volume diverges, since the derivative contains the inverse, Φ^{-1} , as shown in Eq.(2). This realizes a discrete phase transition for a finite system under constant pressure condition. Further, if the physical quantity on which the derivative (2) acts is an analytic function of T and V , the inverse, Φ^{-1} , is the only source of a divergence: none of the partial derivatives, neither $\left. \frac{\partial}{\partial T} \right|_V$ nor $\left. \frac{\partial}{\partial V} \right|_T$, can produce any singularity. This implies that the corresponding exponent of the singularity is determined by the power series expansion of Φ on the isobar and therefore, the exponents can be classified to take universal and exact values, under the assumptions of analytic partition function and isobaric transformations (*c.f.* analogous black hole thermodynamics *e.g.* [29, 30]).

The critical point, (T_c, V_c) , is defined to be a particular

point on the spinodal curve on which the higher order volume derivative of the pressure vanishes:

$$\Phi(T_c, V_c) = -\frac{\partial P(T_c, V_c)}{\partial V} = 0, \quad (7)$$

$$\frac{\partial^2 P(T_c, V_c)}{\partial V^2} = -\frac{\partial \Phi(T_c, V_c)}{\partial V} = 0.$$

The first condition is the definition of the spinodal curve such that, as explained above, the isothermal line is tangent to the isobar, while the second condition implies in a similar fashion that the isothermal line is also tangent to the spinodal curve. Thus, the three curves, isothermal, spinodal and isobar, are all tangent to each other at a critical point. In general, for a certain natural number, $n \geq 2$, we let

$$\frac{\partial^k P(T_c, V_c)}{\partial V^k} = 0 \quad \text{for} \quad 1 \leq k \leq n, \quad (8)$$

and

$$\frac{\partial^n \Phi(T_c, V_c)}{\partial V^n} = -\frac{\partial^{n+1} P(T_c, V_c)}{\partial V^{n+1}} \neq 0. \quad (9)$$

Now, at least locally, around any spinodal point, we invert $P(T, V)$ to express the temperature as a function of P and V . This is justified by the assumption of (6) *via* the implicit function theorem which also ensures that the function $T(P, V)$ is analytic as well. We further fix the pressure to be critical, *i.e.* $P_c = P(T_c, V_c)$. This gives a local expression of the temperature around the critical point as a function of the volume under the fixed critical pressure,

$$T = f_c(V), \quad T_c = f_c(V_c), \quad (10)$$

satisfying

$$P(f_c(V), V) = P_c. \quad (11)$$

The analyticity of the partition function, combined with the implicit function theorem, guarantees that $f_c(V)$ is an analytic function of V . By taking the volume-derivative of the relation (11), which should vanish, it is straightforward to show that the power series expansion of the function, $f_c(V)$, around the critical volume starts at the $(n+1)$ th order,

$$T - T_c = \frac{1}{(n+1)!} \left[\frac{d^{n+1} f_c(V_c)}{dV^{n+1}} \right] (V - V_c)^{n+1} + \text{higher orders}, \quad (12)$$

where, from our assumptions of (6), (8) and (9), the leading order coefficient is nontrivial,

$$\frac{d^{n+1}f_c(V_c)}{dV^{n+1}} = \left[\frac{\partial^n \Phi(T_c, V_c)}{\partial V^n} \right] \left[\frac{\partial P(T_c, V_c)}{\partial T} \right]^{-1} \neq 0. \quad (13)$$

Clearly, Eq.(12) leads to the following isobaric critical exponent:

$$V/V_c - 1 \sim |T/T_c - 1|^{\beta_P}, \quad \beta_P = \frac{1}{n+1}, \quad (14)$$

which implies

$$\left. \frac{dV}{dT} \right|_{P=P_c} \sim |T/T_c - 1|^{-\frac{n}{n+1}}. \quad (15)$$

Similarly, with (9) and (12), the expansion of Φ on the critical isobar starts from the n th order in $V - V_c$ such that, in agreement with (15),

$$\Phi(f(V), V) \sim (V/V_c - 1)^n \sim |T/T_c - 1|^{\frac{n}{n+1}}. \quad (16)$$

Thus, from (2), *any physical quantity given by the temperature derivative along the critical isobar diverges with the universal exponent, $\frac{n}{n+1}$* . This includes the critical exponent of the specific heat under constant pressure:

$$C_P \sim |T/T_c - 1|^{-\alpha_P}, \quad \alpha_P = \frac{n}{n+1}. \quad (17)$$

On the other hand, since the specific heat at constant volume or constant density is finite for any finite system, the corresponding critical exponent should be trivial (if sufficiently zoomed in) [31]:

$$C_V = \text{finite} \quad i.e. \quad \alpha_V = 0. \quad (18)$$

Further, the inverse of Φ gives the critical exponent of the isothermal compressibility on the critical isobar:

$$\kappa_T := -\frac{\partial \ln V(P_c, T)}{\partial P} \sim |T/T_c - 1|^{-\gamma_P}, \quad \gamma_P = \frac{n}{n+1}. \quad (19)$$

This isothermal compressibility exponent, $\gamma_P = \frac{n}{n+1}$, is strictly *less* than one (19), and hence differs from the typical estimations of its constant volume analogue γ_V [3–10]. Nevertheless, the equality of $\alpha_P = \gamma_P$ was reported experimentally for some liquid-crystalline materials, such as n CB and \bar{m} S5 [32].

Finally, from (9), we obtain the *isothermal* critical exponent at the critical temperature, $T = T_c$:

$$P/P_c - 1 \sim |V/V_c - 1|^\delta, \quad \delta = n + 1. \quad (20)$$

Note that, unlike α_P, β_P and γ_P , our last exponent, δ , is *not* defined under the isobaric condition, and yet there should be no ambiguity in the definition (20).

In summary, under the combined hypotheses of analyticity and existence of a spinodal curve, we have the following universal values for the (isobaric) critical exponents [15]:

$$\alpha_P = \gamma_P = \frac{n}{n+1}, \quad \beta_P = \delta^{-1} = \frac{1}{n+1}. \quad (21)$$

They are all determined by a single natural number, n , which should be greater than one, $n = 2, 3, 4, 5, \dots$, and corresponds to the characteristic of a critical point. Henceforth, we name the natural number, *critical index*. As can be easily checked, the isobaric critical exponents satisfy the ‘scaling laws’ [3–10]:

$$\text{Rushbrooke :} \quad \alpha_P + 2\beta_P + \gamma_P = 2, \quad (22)$$

$$\text{Widom :} \quad \gamma_P = \beta_P(\delta - 1).$$

It is worth while to note that, at a generic spinodal point with lower pressure, $P < P_c$, the case of $n = 1$ for (8) and (9) corresponds to the first-order phase transition between the liquid and the gas, which features the superheating and supercooling phenomena. Even at these points, our analysis implies the universal exponent:

$$\alpha_P = \beta_P = \gamma_P = \delta^{-1} = \frac{1}{2}. \quad (23)$$

This has been verified in the liquid-crystalline experiment (without δ) [32] as well as for a relativistic ideal Bose gas (see Figure 5 of [15]).

VAN DER WAALS FLUID: TOY MODEL OF $n = 2$

The first historical example of mean field theory was the van der Waals fluid, which we show here to provide a simple example of the above general consideration. The van der Waals equation reads

$$\left(P_r + \frac{3}{v_r^2} \right) \left(v_r - \frac{1}{3} \right) = \frac{8}{3} T_r, \quad (24)$$

where $P_r = P/P_c$, $v_r = v/v_c$ and $T_r = T/T_c$ are reduced pressure, volume per particle and temperature, such that the critical point is given by $P_r = v_r = T_r = 1$. Around

the critical point, the critical isobar, $P_r \equiv 1$, is given by

$$T_r = \frac{1}{8}(3v_r - 1) \left(1 + \frac{3}{v_r^2} \right) = 1 + \frac{3(v_r - 1)^3}{8v_r^2}. \quad (25)$$

Therefore, near the critical point, $T_r - 1 \sim (v_r - 1)^3$, we get $n = 2$, and hence $\beta_P = \frac{1}{3}$. On the other hand, taking the v_r -derivative of (24), with fixed temperature, gives

$$\left(\frac{\partial P_r(v_r, T_r)}{\partial v_r} - \frac{6}{v_r^3} \right) \left(v_r - \frac{1}{3} \right) + P_r + \frac{3}{v_r^2} = 0, \quad (26)$$

and hence, combined with (25), we get $\gamma_P = \frac{2}{3}$, as follows

$$\begin{aligned} \kappa_T &= - \left. \frac{\partial \ln v_r(P_r, T_r)}{\partial P_r} \right|_{P_r=1} = \frac{v_r^2(v_r - \frac{1}{3})}{(v_r + 2)(v_r - 1)^2} \\ &\sim \frac{1}{(v_r - 1)^2} \sim (T_r - 1)^{-\frac{2}{3}}. \end{aligned} \quad (27)$$

From (24) the critical isothermal relation between pressure and temperature reads, with $T_r \equiv 1$,

$$P_r - 1 = - \frac{(v_r - 1)^3}{(v_r - \frac{1}{3})v_r^2} \sim (v_r - 1)^3. \quad (28)$$

Thus, we note $\delta = 3$. Lastly, in order to obtain α_P , one should first remember that the specific heat at constant volume of any fluid whose equation of state is linear in temperature is equal to that of the classical ideal gas. Thus it is finite and constant, so the corresponding critical exponent should be trivial, *i.e.* $\alpha_V = 0$ (18). On the other hand, the specific heat at constant pressure, C_P , is given by the thermodynamic identity (see *e.g.* [9]),

$$C_P - C_V = -T_r \left(\left. \frac{\partial P_r}{\partial T_r} \right|_{v_r} \right)^2 \left. \frac{\partial v_r}{\partial P_r} \right|_{T_r}, \quad (29)$$

which is proportional to κ_T . Therefore, α_P , the critical exponent of the specific heat under constant pressure takes the same value as $\gamma_P = \frac{2}{3}$. Put all together, the critical point of van der Waals fluid belongs to the class of $n = 2$. Note that the textbook approach to obtain the critical exponents of van der Waals fluid is based on the concept of Maxwell's equal area construction [8, 9, 33], which, we assert, cannot be applied nor defined at the critical point itself. More precisely, the derivation of the conventional critical exponent, " $\beta = \frac{1}{2}$ " is based on the behavior of the *binodal* curve of liquid-vapor coexistence near the critical point, while our isobaric critical exponent, $\beta_P = \frac{1}{3}$, is obtained here by simply fixing the pressure to be critical, $P_r \equiv 1$, in the very van der Waals equation (25).

RESULT & DISCUSSION

We recall the theoretical prediction from analyticity (21), *i.e.* $\alpha_P = \gamma_P = \frac{n}{n+1}$, $\beta_P = \delta^{-1} = \frac{1}{n+1}$. We once more stress that these critical exponents are derived *neither* by assuming the thermodynamic limit *nor* any singularity of the free energy, *but* rather by postulating the analyticity of the partition function, along with the existence of a spinodal curve. Our main result in this work is to verify that such a simple approach appears relevant to the description of the critical phenomena of the liquid-gas phase transition of real fluids: the analyticity-based theoretical prediction is consistent with the high-precision experimental data, REFPROP of NIST [26]. By analyzing the data for twenty major molecules, we are able to classify the critical phenomena of those real fluids in terms of the critical index, $n_- = 2, 3, 4, 5, 6$, for $T < T_c$. For the opposite range of temperature, $T > T_c$, the natural number is universal as $n_+ = 2$, which agrees with both van der Waals fluid and a relativistic ideal Bose gas ($n_- = n_+ = 2$ [15]). We emphasize that it is a nontrivial verification that all the four critical exponents of a given real molecule are fixed by a 'common' natural number, *i.e.* the critical index. Table I and Figures 1, 2, 3, 4 show the main results.

Generically, except C_5H_{10} , we have obtained two distinct critical indices, n_- and n_+ , depending on $T < T_c$ and $T > T_c$. This rather surprising result leads us to conjecture that there exist more than one critical points quite close to each other, such as $(T_{c-}, V_{c-} : n_-)$ and $(T_{c+}, V_{c+} : n_+)$. Further, sufficiently (but not too much) away from the critical point, the critical-isobaric volume derivative of the temperature, $\left. \frac{dT}{dV} \right|_{P=P_c}$ should be positive. On the other hand, from (17), around the critical point it behaves as $\sim (V - V_c)^n$, and thus can be negative for odd n . Thus, if n_- is odd, *e.g.* 3 or 5 from Table I, we suspect that there might exist another critical point, $(T_{c'}, V_{c'} : n')$, amounting to at least three critical points all close to each other. This somewhat complicated multicriticality deserves further investigation.

We may regard our result as an evidence for the finiteness of the real samples in experimental laboratories. Namely, the Avogadro number is still far less than infinity, $6.022 \times 10^{23} \ll \infty$, such that the analyticity persists, at least for $|T/T_c - 1| < 10^{-3}$. Our finding

of the various values of the critical indices for different molecules contradicts the usual identification of the liquid-gas phase transition and the non-analytic 3D Ising model into the same universality class (*c.f.* an analogous discrepancy between liquid crystals and XY model [34]). Nevertheless, it would be still interesting *i)* to investigate if the 3D Ising model can be a good approximation for the range of $|T/T_c - 1| > 10^{-3}$, and *ii)* to identify a conformal field theory description, if any, for each critical index.

ACKNOWLEDGEMENTS

We wish to thank Xavier Bekaert for numerous enlightening discussions and Eric W. Lemmon at NIST for helpful correspondences. This work was supported by Sogang University (Grant No. 201610033.01) and the National Research Foundation of Korea (Grant Nos. 2015K1A3A1A21000302 and 2016R1D1A1B0101519).

*Correspondence and requests for materials should be addressed to both DHK (dohyunkim@sogang.ac.kr) and JHP (park@sogang.ac.kr).

APPENDIX: COMMENT ON GUGGENHEIM'S FITTING

Around the critical point, with $\Phi_c \equiv \Phi(T_c, V_c) = 0$ and from (9), we may expand

$$\Phi(T, V) = \left(\frac{\partial \Phi_c}{\partial T} + \frac{\partial^2 \Phi_c}{\partial T \partial V} \Delta V + \frac{1}{2} \frac{\partial^2 \Phi_c}{\partial T^2} \Delta T \right) \Delta T + \frac{1}{n!} \frac{\partial^n \Phi_c}{\partial V^n} \Delta V^n + \dots, \quad (30)$$

where $\Delta T = T - T_c$, $\Delta V = V - V_c$. Then, near to the critical point, in comparison with the critical isobar (14), the spinodal curve can be approximated by

$$0 < T/T_c - 1 \sim (V/V_c - 1)^n. \quad (31)$$

Our result implies then that, the supercooling ($T < T_c$) and the superheating ($T > T_c$) spinodal curves read separately in terms of the density, $\rho_{\pm} = N/V_{\pm}$,

$$\rho_{\pm}/\rho_c - 1 \sim |T/T_c - 1|^{1/n_{\pm}}. \quad (32)$$

From the empirical result reported in this work, $n_+ < n_-$ (except C_5H_{10}), we expect close to the critical point,

$$|T/T_c - 1|^{1/n_+} \ll |T/T_c - 1|^{1/n_-}. \quad (33)$$

Thus, the difference between the densities of the supercooled gas and the superheated liquid can be approximated by

$$\rho_+ - \rho_- \sim |T/T_c - 1|^{1/n_-}. \quad (34)$$

This is comparable with the renowned Guggenheim's fitting [35] with $n = 3$.

Critical Index (n_- , n_+)	Fluids
(2, 2)	C_5H_{10} (cyclopentane), van der Waals fluid, relativistic ideal Bose gas [15]
(3, 2)	H_2 (hydrogen), O_2 (oxygen), CO (carbon monoxide), C_6H_6 (benzene), C_6H_{12} (cyclohexane), Ne (neon)
(4, 2)	N_2 (nitrogen), Ar (argon), CH_4 (methane), C_2H_4 (ethylene), C_2H_6 (ethane), C_3H_6 (propylene), C_3H_8 (propane), C_4H_{10} (butane), C_4H_{10} (isobutane)
(5, 2)	H_2O (water), CO_2 (carbon dioxide), C_3H_6O (acetone)
(6, 2)	4He (helium-4)

TABLE I. Classification of the 20 major fluids plus the relativistic ideal Bose gas and the van der Waals fluid, according to the critical indices: n_- for $T < T_c$ and n_+ for $T > T_c$. Note the universal value, $n_+ = 2$. We have determined the critical indices from the experimental data of NIST (REF-PROP) [26] especially over the reduced temperature range, $10^{-5} < |T/T_c - 1| < 10^{-2}$.

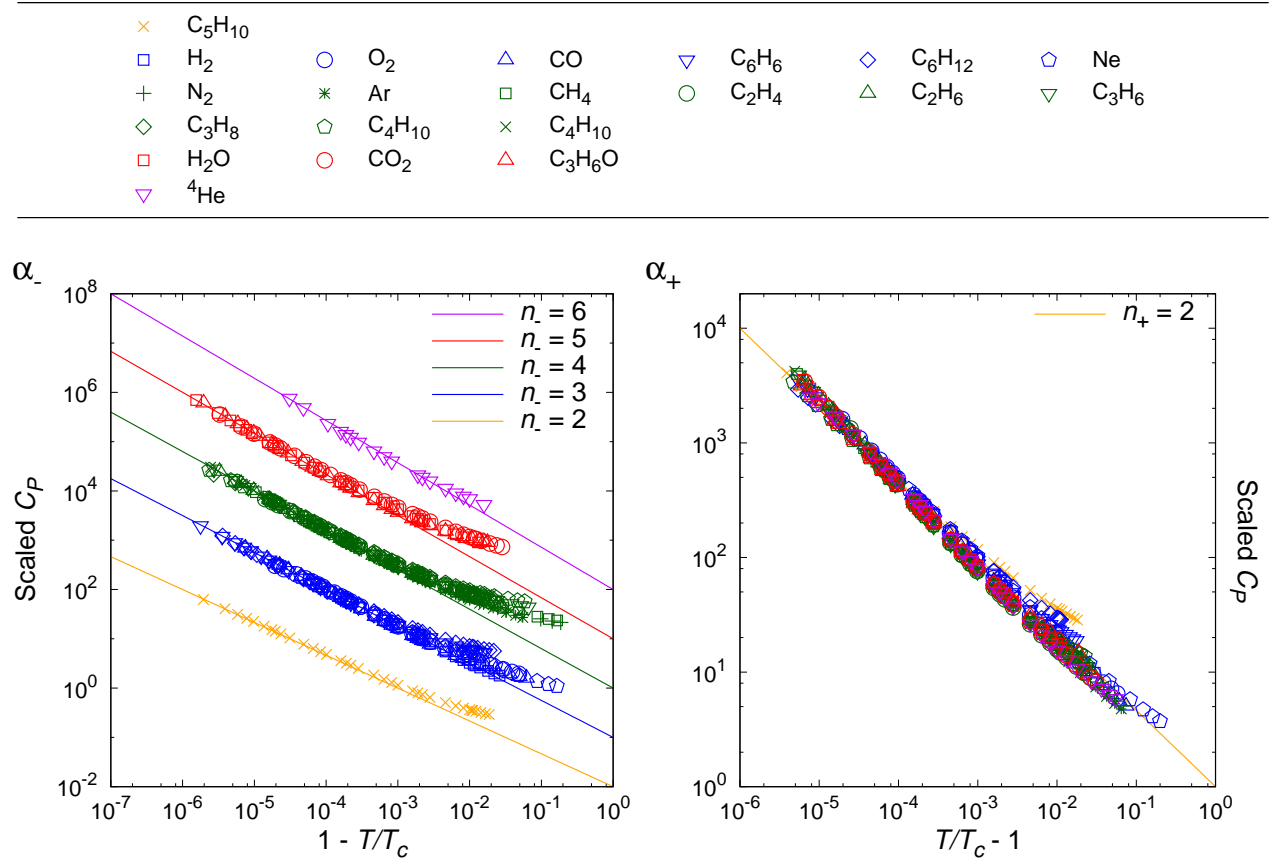


FIG. 1. Critical exponent, $\alpha_P = \frac{n_-}{n_- + 1}$: $n_- = 2, 3, 4, 5, 6$ for $T < T_c$ and $n_+ = 2$ for $T > T_c$

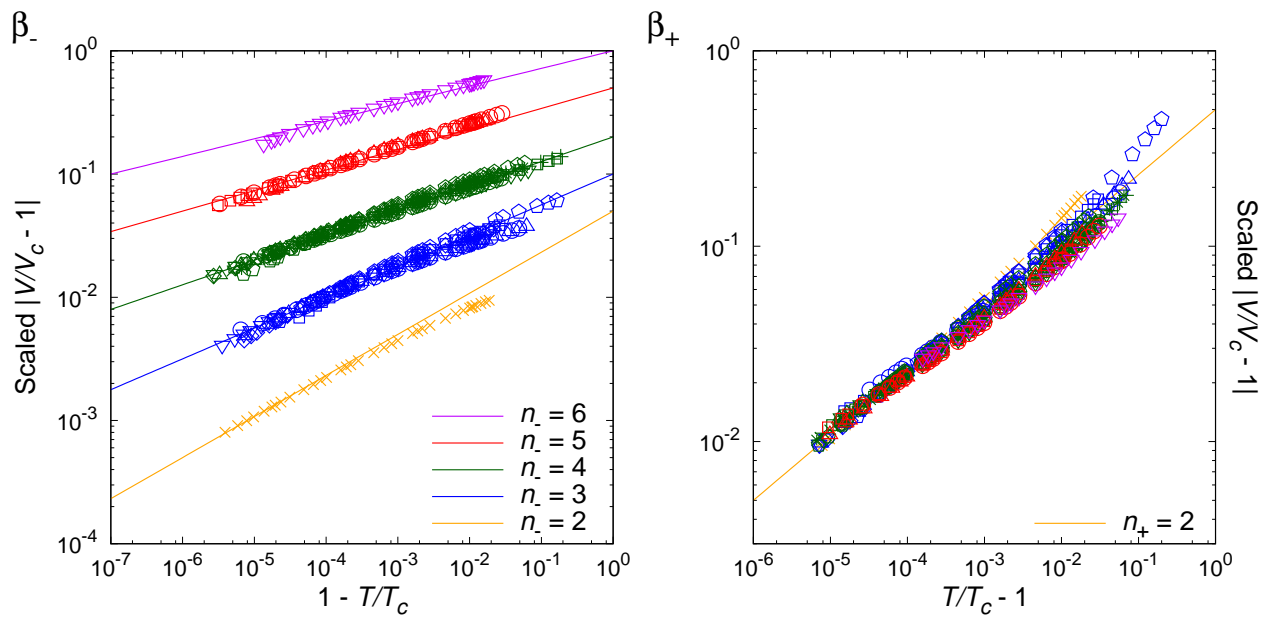


FIG. 2. Critical exponent, $\beta_P = \frac{1}{n_- + 1}$: $n_- = 2, 3, 4, 5, 6$ for $T < T_c$ and $n_+ = 2$ for $T > T_c$

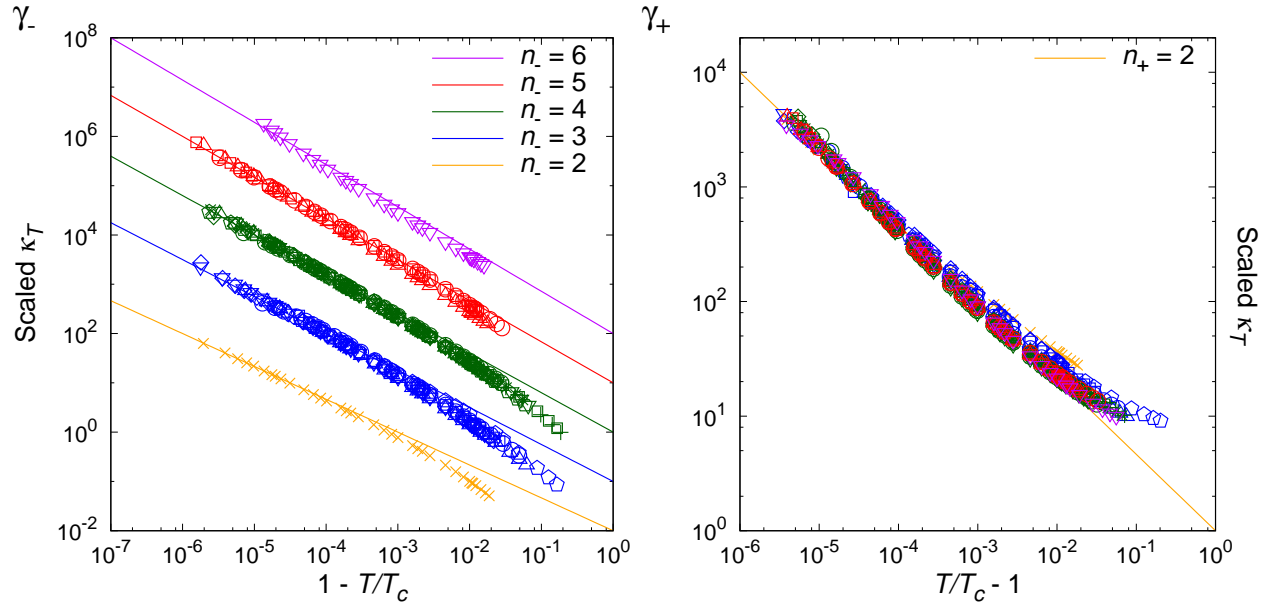


FIG. 3. Critical exponent, $\gamma_P = \frac{n}{n+1}$: $n_- = 2, 3, 4, 5, 6$ for $T < T_c$ and $n_+ = 2$ for $T > T_c$

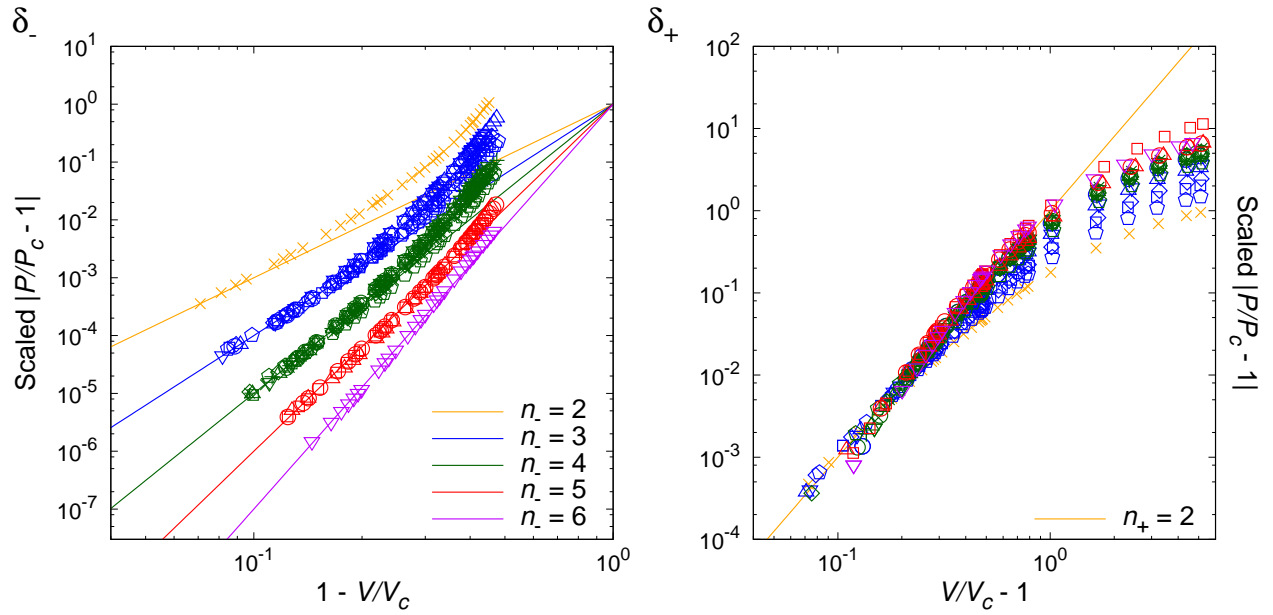


FIG. 4. Critical exponent, $\delta = n + 1$: $n_- = 2, 3, 4, 5, 6$ for $V < V_c$ and $n_+ = 2$ for $V > V_c$

-
- [1] P. W. Anderson, “More Is Different,” *Science* **177**, 393 (1972).
- [2] C. N. Yang and T. D. Lee, “Statistical Theory of Equations of State and Phase Transitions. I. Theory of Condensation,” *Phys. Rev.* **87** 404 (1952); “Statistical Theory of Equations of State and Phase Transitions. II. Lattice Gas and Ising Model,” *Phys. Rev.* **87** 410 (1952).
- [3] M. E. Fisher, “The theory of equilibrium critical phenomena,” *Rep. Prog. Phys.* **30** 615 (1967).
- [4] P. Heller, “Experimental investigations of critical phenomena,” *Rep. Prog. Phys.* **30** 731 (1967).
- [5] L. P. Kadanoff, *et al.*, “Static Phenomena Near Critical Points: Theory and Experiment,” *Rev. Mod. Phys.* **39** 395 (1967).
- [6] H. E. Stanley, *Introduction to Phase Transitions and Critical Phenomena* Oxford University Press, (1971).
- [7] K. G. Wilson and J. Kogut, “The renormalization group and the ϵ expansion,” *Phys. Rep.* **12** 75 (1974).
- [8] K. Huang, *Statistical Mechanics* Wiley, (1987).
- [9] N. Goldenfeld, *Lectures on Phase Transitions and the Renormalization Group* Addison-Wesley, (1992).
- [10] L. P. Kadanoff, *Statistical Physics: Statics, Dynamics and Renormalization* World Scientific, (2000).
- [11] L. P. Kadanoff, “More is the Same; Phase Transitions and Mean Field Theories,” *J. Stat. Phys.* **137**, 777 (2009).
- [12] F. London, *Superfluids* Dover Publications, Inc. (1954), Vol. II, Part 7.
- [13] Y. Imry, D. J. Bergman and L. Gunther, “Bose-Einstein Condensation in Two-Dimensional Systems,” *Low Temperature Physics-LT 13* Springer US (1974), Vol. 1, p. 80.
- [14] A. N. Chaba and R. K. Pathria, “Bose-Einstein condensation in a two-dimensional system at constant pressure,” *Phys. Rev. B* **12** 3697 (1975).
- [15] J.-H. Park and S.-W. Kim, “Existence of a critical point in the phase diagram of ideal relativistic neutral Bose gas,” *New J. Phys.* **13** 033003 (2011).
- [16] J. W. Gibbs, *The Scientific Papers of J. Willard Gibbs* Dover Publications, Inc. New York, (1961).
- [17] V. P. Skripov, *Metastable liquids* J. Wiley (1973).
- [18] D. Chandler, *Introduction to Modern Statistical Mechanics* Oxford University Press (1987).
- [19] E. H. Chimowitz, *Introduction to Critical Phenomena in Fluids* Oxford University Press (2005).
- [20] J. P. O’Connell and J. M. Haile, *Thermodynamics: Fundamentals for Applications* Cambridge University Press (2005).
- [21] M. Scott Shell, *Thermodynamics and Statistical Mechanics: An Integrated Approach* Cambridge University Press (2015).
- [22] J.-H. Park and S.-W. Kim, “Thermodynamic instability and first-order phase transition in an ideal Bose gas,” *Phys. Rev. A* **81** 063636 (2010).
- [23] I. Jeon, S.-W. Kim and J.-H. Park, “Isobar of an ideal Bose gas within the grand canonical ensemble,” *Phys. Rev. A* **84** 023636 (2011).
- [24] W. Cho, S. W. Kim and J.-H. Park, “Two-dimensional Bose-Einstein condensate under pressure,” *New J. Phys.* **17** 013038 (2015).
- [25] J.-H. Park, “How many is different? Answer from ideal Bose gas,” *J. Phys. Conf. Ser.* **490** 012018 (2014), [arXiv:1310.5580 [cond-mat.stat-mech]].
- [26] E. W. Lemmon, M. L. Huber, M. O. McLinden, NIST Reference Fluid Thermodynamic and Transport Properties Database (REFPROP): Version 9.1, National Institute of Standards and Technology (NIST), Standard Reference Data Program, Gaithersburg, 2013. (<https://www.nist.gov/srd/refprop>)
- [27] For examples, the uncertainty in pressure of nitrogen in the critical region is estimated to be 0.02%. The uncertainty in pressure of water in the critical region is 0.1%. The uncertainty in heat capacities of argon is within 0.3% for the vapor and 2% for the liquid. The uncertainties in vapor pressure of helium are less than 0.02% and for the heat capacities are about 2%. The detailed information on the data can be obtained by downloading the (commercially available) REFPROP database program *via* its website [26].
- [28] In order to identify any spinodal curve, or more generically to see nontrivial quantum effects, one should rather keep the analyticity of the partition function and aim to perform not a somewhat hasty approximate integral but an exact discrete sum over countable quantum states, *c.f.* N. A. Nekrasov, “Seiberg-Witten prepotential from instanton counting,” *Adv. Theor. Math. Phys.* **7** 831 (2003).
- [29] A. Chamblin, R. Emparan, C. V. Johnson, and R. C. Myers, “Holography, thermodynamics and fluctuations of charged AdS black holes,” *Phys. Rev. D* **60** (1999) 104026.
- [30] A. Mandal, S. Samanta and B. R. Majhi, “Phase transition and critical phenomena of black holes: A general approach,” *Phys. Rev. D* **94** (2016) 064069.
- [31] On the other hand, if appropriately zoomed out, it might be possible to observe pseudo-thermodynamic-limiting behavior, with finite peak.
- [32] A. Zywockinski and S. A. Wiczorek, “Critical Exponents for Thermal Expansion and Isothermal Compressibility near the Nematic to Smectic-A Phase Transition,” *J. Phys. Chem. B* **101** 6970 (1997). Note the different no-

tations used in this paper, *e.g.* $\kappa_T^{ours} \equiv \beta_T^{theirs}$.

- [33] J. M. H. Levelt Sengers, “From Van der Waals’ equation to the scaling laws,” *Physica* **73** 73 (1974).
- [34] C. W. Garland and G. Nounesis, “Critical behavior at nematic–smectic–A phase transitions,” *Phys. Rev. E* **49** 2964 (1994).
- [35] E. A. Guggenheim, “The Principle of Corresponding States,” *J. Chem. Phys.* **13**, 253 (1945).